Chapter

Applications of Titanium Dioxide Materials

Xiaoping Wu

Abstract

Titanium dioxide (TiO_2) is a stable, non-toxic inorganic material. Because of very high refractive index, TiO_2 has been widely used as a white pigment. The optimal particle sizes of TiO_2 for pigment applications are around 250 nm. The pigmentary applications of TiO_2 can be found in many common products such as paints, plastics, paper and ink. Global titanium dioxide pigment sales have reached several million tons annually. Titanium dioxide is also a semiconducting material. When excited by photons which have energy equal to or higher than the band gap of TiO_2, electron/hole pairs can be generated. The dynamics of the photo-generated electron/hole pairs of TiO_2 is fundamentally important to its photocatalytic properties. More recently, nano-structured TiO_2 has raised a great deal of interests in research after the discoveries of the important potentials for applications. The enormous efforts have been put in the preparation, characterization, scientific understandings, and modifications of the photocatalytic properties of TiO_2. The applications of nano-structured TiO_2 can be now found in a wide range of areas including electronic materials, energy, environment, health & medicine, catalysts, etc. This chapter has discussed and highlighted the development of the applications of titanium dioxide materials in many of those areas.

Keywords: Titanium dioxide, Applications, Pigment, Nano-structured

1. Introduction

Titanium dioxide (TiO_2) is an inorganic substance that is used extensively as a white pigment. Compared with many other inorganic pigments, TiO_2 has the advantages of high stability, being non-toxic, and low cost. TiO_2 have three polymorphs: anatase, rutile and brookite, but only anatase and rutile crystal forms have been useful as pigment. Both anatase and rutile crystals have very high refractive indices, and their particles can scatter visible light almost completely [1]. The optimum particle size of TiO_2 for pigment applications is around 250 nm. In the early application of TiO_2 as pigment, it was found that paint faded more rapidly than others when painted films were exposed to the Sun and ultraviolet (UV) light. Coating with inorganic compounds such as alumina or silica suppressed the catalytic activity on the surface and improve the weather resistance, leading titanium dioxide in wide applications as white pigment. Global titanium dioxide pigment sales were about 6 million tons in 2017 and the growth trend of global titanium dioxide pigment sales is continuing over the recent years [2].

In the 60s of the last century, scientists studied the photo-induced phenomena on the solids of TiO_2 and ZnO under UV light irradiation [3–5]. In the early 1970s, research on photocatalysis by TiO_2 got wide attention due to the historic discovery of the electrochemical water splitting by use of TiO_2 [6]. In the 1990s, photocatalytic research of TiO_2 had made progress in the practical applications of TiO_2 in the decomposition of harmful organic materials [7, 8]. A function of super hydrophilicity of TiO_2 was also discovered [9]. Since the beginning of this century, nano-structured TiO_2 has attracted extensive interests. When the particle sizes of TiO_2 are reduced down to the nano-meter scale (generally in 1–100 nm), the surface characteristics and surface areas of TiO_2 have changed dramatically. The new or enhanced physical and chemical properties of nano-structured TiO_2 begin to emerge. The photocatalytic property of nano-structured TiO_2 has been greatly enhanced because of the changes in the surface characteristics and surface areas. Quantum effects of nano-structured TiO_2 can also have a role to play, affecting its photocatalytic, optical or electronic properties. As the results of academic and industrial research in recent years, enormous progresses have been made in the preparation, characterization, and scientific understandings of nano-structured TiO_2. Nano-structured TiO_2 have begun to find applications in a wide range of areas including electronic materials, energy, environment, health & medicine, sensors, catalysts, etc.

TiO_2 pigment is industrially produced from titanium containing ores by using a Chloride or Sulfate process [1, 10]. Nano-structured TiO_2 are made in the different ways, depending on the material characteristics required for the specific applications. A number of innovative fabrication methods of nano-structured TiO_2 materials have been developed and are used for different applications. These methods can be broadly classified as the liquid phase or the gas phase methods. Nano-particles, nano-wires, nano-tubes, two or three-dimensional nano-structured TiO_2 materials can also be fabricated for different applications [11–18].

This chapter will discuss and highlight the recent development of applications of titanium dioxide as pigment and as functional materials in the areas of energy, environment, catalyst, and biomedicine.

2. Application of titanium dioxide as pigment

2.1 Light scattering of pigmentary TiO_2

The main use of titanium dioxide is white pigment, because it absorbs almost no incident light in the visible region of the spectrum (380–700 nm). Titanium dioxide has a strong light scattering power, and scatters incident light in three ways: surface reflection, refraction and diffraction in the crystal [1]. When the refractive index difference between titanium dioxide and medium increases, the reflected light increases and complies with Eq. (1):

$$R = \frac{(n_p - n_m)^2}{(n_p + n_m)^2} \tag{1}$$

n_p and n_m are the refractive index of pigment and medium, respectively [1]. Titanium dioxide has a high refractive index (refractive index of rutile and anatase titanium dioxide is 2.70 and 2.55 respectively) [19]. These high refractive index values enable the rutile and anatase TiO_2 pigments to have much greater hiding power in coatings or in plastics, making TiO_2 to be a much better pigment than the other chemical substances. Therefore, under the same conditions, only less titanium dioxide is needed to form a coating, which is white and opaque. Studies have shown that the optical properties of titanium dioxide pigments are related to their particle size, and the optimum of particle size of pigmentary titanium dioxide is around 250 nm [1].

2.2 Application areas

Pigmentary TiO_2 is inert, non-toxic, stable and less costly. Over 50 percent of all TiO_2 pigment produced is consumed by the coatings industry, and approximately a quarter by the paper industry. Eleven per cent goes into plastics; remaining a few percent into inks and other end-uses [20]. Titanium dioxide particles optimized with particle size and surface treatments have excellent hiding power, brightness, and other important features such as resistance to chemical degradation. Rutile pigment is more resistant to UV light than anatase, and is preferred for paints, plastics, especially for the applications in outdoor conditions. Anatase pigment is less abrasive and is used mainly in indoor paints and in paper manufacture. TiO_2 is surface treated with one or more inorganic oxides such as alumina, silica, zirconia or a combination of these inorganic oxides, and organic compounds such as polyhydric alcohol to have the required properties of dispersion, photoactivity, and opacity required for a specific application [21].

In coating applications, a relatively high quantity of TiO_2 pigment must be used to achieve desirable hiding effect on the coating subtracts, because coatings of titanium dioxide are usually in the form of very thin layers. The pigment volume concentration (PVC) is practically used to specify the amount of TiO_2 in a coating. Different types of paints containing TiO_2 pigment will have different levels of PVC, depending on different coating applications. TiO_2 coatings are used to cover a wide range of surfaces, including indoor and outdoor building, wood products, metal objects, domestic and industrial equipment [21].

In plastics applications, titanium dioxide pigment is used to opacify plastic materials. In some applications, TiO_2 is used to improve photodurability. The requirements for TiO_2 in plastics are good dispersibility in a polymer system and good heat stability. Hydrophobic organic surface treatments on the pigments are utilized to facilitate their dispersion in the viscous molten plastic resin. These are often silicone oils and other organic compounds for specialized uses. In many plastics applications, a blue undertone is also desirable to mask an intrinsic yellowness in the color of the resin or a slight degradation that occurs during the high-temperature processing. For this reason, plastics pigments often have a smaller crystal size than those for coatings applications [19].

The amount of titanium dioxide used in paper industry is the third largest after coating and plastic industries [20]. Although other white pigments can be used in paper industry, the production of high quality papers must use titanium dioxide as pigment. Titanium dioxide imparts desirable brightness and opacity to high-quality papers. Papers containing titanium dioxide pigment have high strength and have appearance to be white, shiny, thin and smooth. Because photochemical stability is not as critical in paper as in paint, both anatase and rutile pigments are widely be used in paper industry.

In inks applications, performance requirements for TiO_2 pigment are different from coatings, plastics and paper. Inks are usually applied to produce a much thinner film on a surface than a general coating. It is very important to choose titanium dioxide particles with good shape, suitable size and size-distribution, smooth surface and non-angular. The type of TiO_2 can also affect the rheology, abrasiveness, gloss and redispersibility for ink products and applications.

TiO_2 is also widely used as a pigment for coloring of different products in pharmaceuticals and cosmetics industries. The characteristics of titanium dioxide provide interesting colors and allow new properties to pharmaceuticals with very small amounts of pigments. There are many products in this field that contain titanium dioxide, including: shampoos, creams, sunscreens, toothpaste, etc. [10].

3. Applications TiO_2 in energy generation and storage

With the special physical and chemical properties, nano-structured titanium dioxide has shown a number of promising application prospects in energy generation and storage. These include: solar cells, hydrogen production, and lithium battery [22–24].

3.1 Application of TiO_2 in dye-sensitized solar cell (DSSC)

The solar energy is a clean, abundant and renewable energy [25]. The current technology for the conversion of sunlight to electrical power is predominately silicon-based solid state solar cells. In recent years, the new semiconducting material-based solar cells have emerged to offer the possible alternative photovoltaic technology with prospect of cheap fabrication and flexibility [26–28]. Nano-structured TiO_2 has been the main semiconducting material for this new generation of solar cells. In this technology, an electron sensitizer absorbing in the visible is used to inject charge carriers across the semiconductor-electrolyte junction into TiO_2 to enhance the conversion efficiency from solar energy, because TiO_2 with its band gap of 3.2 electronvolt (eV) absorbs only the ultraviolet part of the solar energy. This type of solar cells is therefore called dye-sensitized solar cells (DSSCs). The dye-sensitized solar cells (DSSCs) have exhibited high performance and have the potential to be low-cost [29–33].

Figure 1 illustrates the working principle of a dye-sensitized solar cell. The dye-sensitized solar cell consists of two electrodes, a dye-sensitized nano-structured TiO_2 mesoporous layer, and a liquid electrolyte containing redox system (I^-/I_3^-). The nano-structured TiO_2 mesoporous layer with a monolayer of the charge transfer dye at its surface is placed in contact with a redox electrolyte. Under solar

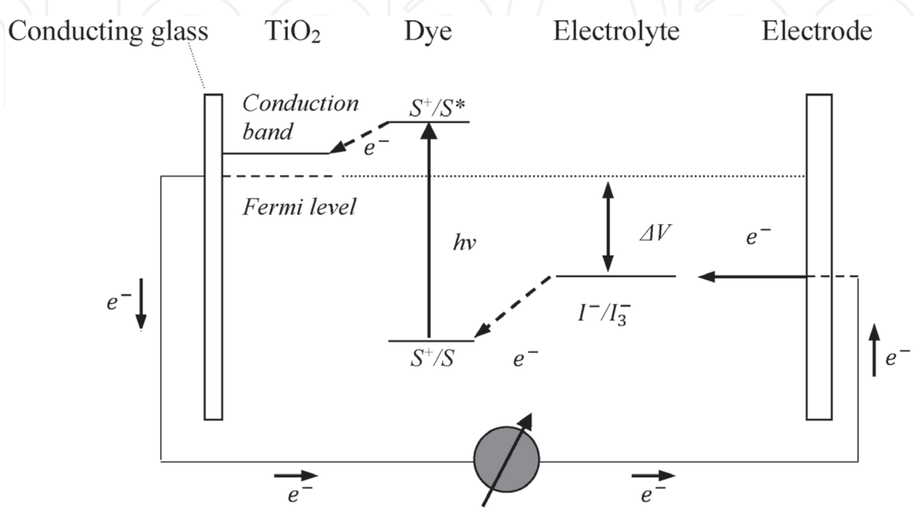

Figure 1.
Working principle of a dye-sensitized solar cell. S, S⁺, *and* S* *represent dye sensitizer, oxidized dye sensitizer, and excited dye sensitizer, respectively.* ΔV *is the difference between Fermi level and electrochemical potential of the electrolyte.*

irradiation, the charge transfer dye injects electrons into the conduction band of TiO_2, and the electrons are conducted to the external circuit to produce electric power. The original state of the dye is subsequently restored by an electron donation from the electrolyte (for example, an organic solvent containing a redox system of iodide/triiodide couple).

The nano-structured TiO_2 mesoporous layer in a dye-sensitized solar cell has a much larger surface area available for the dye-chemisorptions. The kinetic processes occurring in a dye-sensitized solar cell have been profoundly changed as a result of using nano-structured TiO_2. Solar energy-to-electricity conversion efficiencies of DSSCs have been increased. The record for the highest certified single cell and DSSCs module efficiencies are 11.9% and 8.8%, respectively [34].

More recently, TiO_2 is used in a new type of solar device so-called pervoskite solar cells. As in DSSCs, TiO_2 is used as a mesoporous layer. However, instead of using organic dye in DSSCs, organic lead complex (for example, $CH_3NH_2PbI_3$) is used to inject electrons into the conduction band of TiO_2. In a short period of the recent few years, the reported efficiency of pervoskite solar cells was 9.7% initially, and then 12.0% [35, 36]. Further progress was made with efficiencies above 15.0% [37]. The record for the highest certified single cell and minimodule efficiencies are 20.9% and 16.0%, respectively [34].

3.2 Application of TiO_2 in hydrogen production

In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water on a TiO_2 electrode under UV light [6, 38, 39]. Compared with other photocatalysts, TiO_2 is much more promising as it is stable, non-corrosive, environmentally friendly, abundant and cost effective. **Figure 2** illustrates the mechanism of the photocatalytic hydrogen production by TiO_2 semiconducting materials. When excited by photons which have energy equal to or higher than their band gap (*Eg*), electrons (e^-) in valence band (VB) of TiO_2 are promoted from to the conduction band (CB). Simultaneously, Holes (h^+) create in VB of TiO_2. The process of generating (e^-) and (h^+) in TiO_2 with excitation by photons is described with Eq. (2):

$$TiO_2 + hv \rightarrow e^- + h^+ \tag{2}$$

The photo-generated (e^-) and (h^+) in TiO_2 can recombine, releasing energy in the form of heat or photons. The photo-generated (e^-) and (h^+) that migrate to the surface of TiO_2 without recombination can reduce and oxidize H_2O molecules adsorbed on the surface of TiO_2 to generate H_2 and O_2.

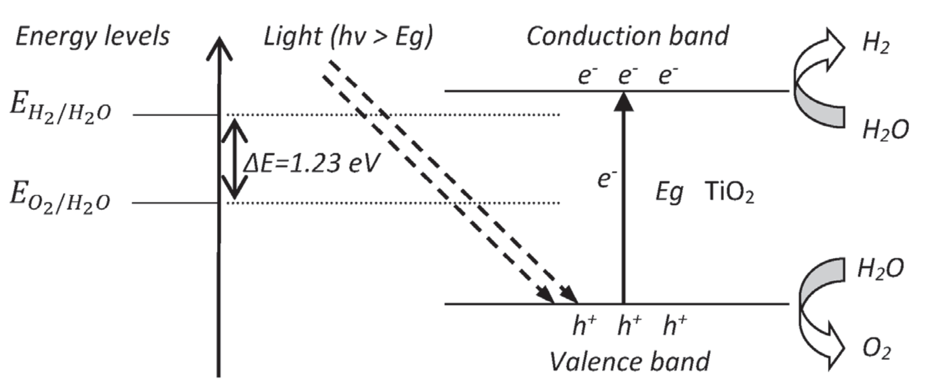

Figure 2.
Illustration of mechanism of photocatalytic hydrogen production by TiO_2.

As can be seen in **Figure 2**, the conduction band level of TiO_2 is more negative than the hydrogen production level (E_{H_2}/H_2O), and the valence band is more positive than water oxidation level (E_{O_2}/H_2O). ΔE, representing the energy difference between hydrogen production level and water oxidation level, is 1.23 eV. The conduction and valence band levels of TiO_2 meet the requirement for hydrogen production. As in dye-sensitized solar cell, nano-structured TiO_2 can enhance the photocatalytic reactions for the generation of hydrogen by a number of ways. For example, much more surface area per mass is available for adsorption of water due to the decreased particle sizes of TiO_2 nano-particles. The surface of TiO_2 nano-particles can also become more reactive because much higher portion of atoms exists at the surface. Furthermore, the quantum effect of TiO_2 nano-particles becomes more significant as particle size of TiO_2 is getting very small. Nano-structured TiO_2 has been known to be stable, chemically inert, and low cost.

Despite many advantages of using TiO_2 for photocatalytic hydrogen production, the efficiency using solar energy for water-splitting by TiO_2 is still low, and is currently not been used for industrial scale of hydrogen production. The low energy conversion efficiency of TiO_2 in water-splitting is believed to be caused by the wasteful recombination of electron/hole pairs, backward reaction of combining hydrogen and oxygen into water, and limitations for TiO_2 to utilize visible light due to its large band gap. Research has been carried out to produce nano-structured TiO_2 with a narrower band gap in order to utilize visible-light energy more efficiently. Progresses have been made in modifying the band gap of nano-structured TiO_2 by means of metal loading, ion doping, metal ion-implantation, dye sensitization and composite TiO_2. Noble metals, such as Pt, Au, Pd, and Ag, have been reported to be very effective in enhancing TiO_2 photocatalysis [40–43]. Carbon-doped nano-structured TiO_2 have showed much more efficient water splitting under visible-light illumination [44]. A study using a dye sensitizer for photocatalytic hydrogen production was investigated [45]. A visible light absorber, C_3N_4, has been coupled to many wide-band gap semiconductors to improve solar harvesting. A 50 wt % C_3N_4/TiO_2 junction was found to double H_2 evolution compared to pure C_3N_4 under visible irradiation [46].

3.3 Application of TiO_2 in energy storage

Lithium-ion batteries are a type of rechargeable batteries commonly used in consumer electronics. Lithium ion battery system and technology has been a revolutionary change in the field of power supply battery. Anode materials based on titanium oxides are the promising candidates as alternative materials to carbonaceous anodes due to advantages in terms of cost, safety and toxicity [47, 48]. TiO_2 also exhibits excellent structural stability, high discharge voltage plateau (more than 1.7 V versus Li^+/Li), and excellent cycling stability [49, 50].

Typically the Li^+ insertion–extraction reaction for TiO_2 polymorphs occurs according to reaction (3):

$$xLi^+ + TiO_2 + xe^- = LixTiO_2 \tag{3}$$

x can range between 0 and 1, depending strongly on the polymorph, particle size, and morphology of TiO_2. The maximum theoretical capacity is 335 mAh g^{-1} which corresponds to x = 1. This makes TiO_2 a highly competitive alternative to graphite anodes having a theoretical capacity of 372 mAh g^{-1} [51–53]. However, TiO_2 has limitations, such as low capacity, low electrical conductivity, and poor rate capability. Strategies have been developed to address the issues of TiO_2-based anodes. These include the use of multi-dimensional nanostructured TiO_2, composite and coating materials, and element doping.

One dimensional anatase TiO_2 nanofiber anodes were used as an anode active material in Li ion batteries and exhibited a high lithium storage capacity, a stable cycle life, and good rate capability [54]. Two dimensional TiO_2 nanosheets have been shown to exhibit the superior capacities, improved cycling stability and rate capabilities, owing to unique exposed facets, shortened path, and reserved porous structures [55–57]. Nanostructured TiO_2 is a low voltage insertion host for Li and a fast Li insertion/extraction host [58, 59]. These characteristics provide nanostructured TiO_2 a potential anode material for high-power Li-ion batteries. Studies on the use of nanostructured TiO_2 as anode with $LiCoO_2$ cathode demonstrated specific capacity of 169 mAh g^{-1} [60]. Xu, et al. investigated electrochemical performance of TiO_2-coated $LiCoO_2$ and $LiMn_2O_4$ in different potential regions [61]. Mechanically blended composite of nanosized TiO_2 and carbon nanotubes (CNTs) has been used as potential anode materials for Li-ion batteries. It was found that the TiO_2/CNTs nanocomposites exhibited an improved cycling stability and higher reversible capacity than CNTs [62, 63]. Metal oxide coatings containing TiO_2 can efficiently improve the capacitive performance of the materials through synergistic effects in an electrode system [64–67].

4. Application of TiO_2 in environment protection

4.1 Fundamental

Excitation of TiO_2 with UV light with energy greater than the band gap (>3.2 eV) promotes electrons from valence band into the conduction band and generates electron/hole pairs [68, 69]. **Figure 3** illustrates the mechanism of generating reactive radicals from TiO_2 under irradiation of UV light. The conduction band electrons e^- can reduce molecular oxygen to generate ($O_2^{\bullet -}$) superoxide radicals, and valance band holes h^+ is positive enough to generate ($OH^\bullet$) radicals from H_2O or OH^- on TiO_2 surface. $OH^\bullet$ radicals have the strongest oxidation potential. Superoxide radicals ($O_2^{\bullet -}$) have moderate oxidation potentials, but their diffusion distances can reach up to hundreds of micrometers [70]. Both radicals are very reactive, and they attack the organic matter present or near the surface of TiO_2 to degrade toxic and bio-resistant compounds or species into CO_2, H_2O, etc. [69, 71].

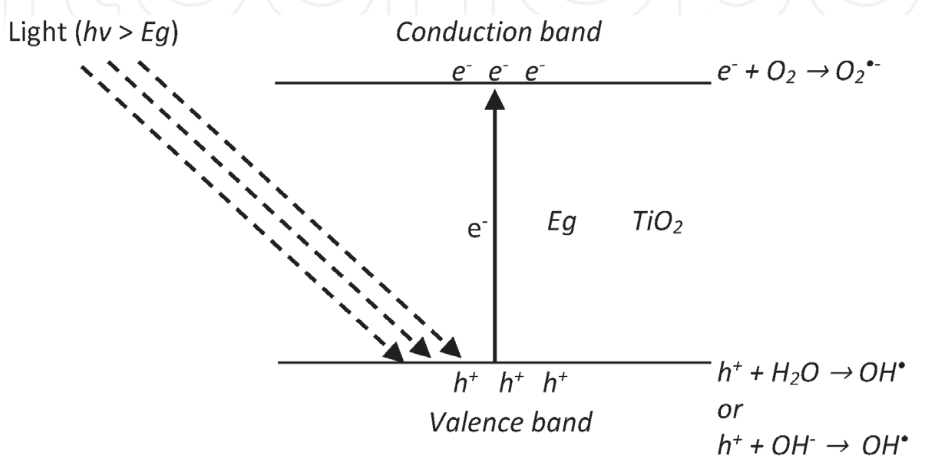

Figure 3.
Mechanism of generating reactive radicals ($OH^\bullet$) and superoxide ($O_2^{\bullet -}$) from TiO_2 under irradiation of UV light.

The generation of reactive radicals ($OH^{\bullet}$) and ($O_2^{\bullet -}$) is affected by the crystalline state, and properties such as surface area and particle size. Although anatase and rutile have the similar band gaps, anatase has shown to have more rapid rate in photo-degradation of organic or bio-resistant compound than rutile [72, 73]. Therefore, nano-structured anatase TiO_2 is often used as a catalyst in photo-degradation applications.

4.2 Self-clean and antibacterial uses of TiO_2

One application, which is commercially successful, is the nano-structured TiO_2 material for self-clean and antibacterial uses [68, 74, 75]. Many nano-structured TiO_2 material based products have been used as construction materials [76–82]. Self-clean application is based on the actions of sunlight, rainwater, and photocatalytic properties of TiO_2. Under the irradiation of sunlight, adsorbed organic materials like oil can be decomposed by hydroxyl radicals on the surface of TiO_2. Because of the hydrophilic property of TiO_2 surface, contaminates and dust can be washed away off by rainwater. Tiles containing nano-structured TiO_2 have been used to construct photocatalytic surface to decompose bacteria and viruses on the surface or bacteria floating in the air as they come in contact with surface.

Studies have shown that the photocatalytic properties of TiO_2 can sometimes be enhanced by doping TiO_2 with different elements. For example, TiO_2 nano-particles containing Ag^+ have been widely used in antibacterial plastics and coatings [83–85]. Fe or Sb-doped TiO_2 have been used to make coatings with high antibacterial property [79, 80].

Nano-structured self-clean glass is now an important commercial product. Pilkington Glass has developed the first self-cleaning windows. The window glass is coated with a very thin and transparent TiO_2 layer to have the properties of photocatalysis and hydrophilicity on the glass surface. Photocatalysis of TiO_2 break down the organic dirt adsorbed onto the window in sunlight, and the decomposed organic species is washed away efficiently by rain or other water in the form of thin layer instead of droplets [86].

4.3 Application of TiO_2 in water-treatment

Another important application of nano-structured TiO_2 is in the water-treatment, utilizing its photocatalytic properties [87–92]. Research of using nano-structured TiO_2 for water-treatment has been very active in recent years. TiO_2 has been used in the photocatalytic decomposition of organic dyes in waste water, and organic pollutants such as pesticides, dyes and pharmaceuticals in other contaminated water [93, 94]. The photocatalytic decomposition of organic matters in water are all based on the mechanism of the generation of highly reactive radicals ($OH^{\bullet}$) and superoxide ions ($O_2^{\bullet -}$) in TiO_2 under UV irradiation, as illustrated in **Figure 3**. TiO_2 has been considered to be the best choice to be used as photo-catalysts, as TiO_2 is chemically inert, and cheap to manufacture and to apply.

The complete separation and recycling of TiO_2 fine particles is important for the practical applications. A number of innovative methods have been developed for this purpose. For example, fixing TiO_2 nano-particles on supports such as glass plates, aluminum sheets, and activated carbon are investigated to recycle the catalyst [95], or developing TiO_2 catalyst system which can be separated from reaction liquid by applying external magnetic field [96, 97].

Because TiO_2 and many other semiconductors have the large band gaps, the application of photocatalytic water treatment using TiO_2 is limited by its relatively low efficiency. To improve photocatalytic efficiency of TiO_2 for water treatment, as well as other photocatalytic applications, Enormous research has been carried out to extend the photocatalytic response of TiO_2 into the visible range [98]. One of the strategies for improving photocatalytic efficiency for water treatment is to modify the band gap of TiO_2 by incorporation of other ions into TiO_2 structure, through metal and non-metal doping, metal implantation, noble metal loading, and others [99–104].

5. Application of TiO_2 in catalyst

TiO_2-based composite materials have been widely used as catalysts [105–107]. TiO_2 is used as support in commercial V_2O_5-WO_3/TiO_2 catalysts for the selective catalytic reduction (SCR) of NOx. In SCR technology, highly undesirable NOx acid gas emissions from various industrial sources are reduced to harmless N_2 and H_2O. The V_2O_5-WO_3/TiO_2 catalysts are widely used in commercial applications because of their excellent thermal stability and lower oxidation activity for the conversion of SO_2 to SO_3 [108, 109]. The V_2O_5-WO_3/TiO_2 catalysts have become the most widely used industrial catalysts for these SCR applications since the introduction of this technology in the early of 1970s [110].

TiO_2 has the potential to induce the reductive chemical transformation. The reductive photocatalysis of ethyne and ethene have been reported [111–113]. TiO_2 have been used as a useful catalyst for the reduction of carbonyl compounds such as aldehydes or ketones, nitro compounds, imines and for the some of the chemical transformations involving redox processes. Photocatalysis on TiO_2 is a light-driven redox reaction. Redox reactions can be induced by electrons (e^-) generated in conduction band (CB) and holes (h^+) simultaneously generated in valance band (VB) under the irradiation of light. The electrons in the conduction band are readily available for transferring while the holes in the valence band are open for donations [114]. The photocatalytic reduction of an electron acceptor can be carried out in the presence of a large excess amount of electron donors such as alcohols or amines, which are used to scavenge (h^+). Oxygen (O_2) is a competitive electron acceptor, and can influence the reduction reaction. Therefore, the reductive chemical transformation should be generally performed in an O_2 free environment. Under these conditions, a photocatalytic reduction proceeds through transferring electrons (e^-) in CB or trapped at surface defects of TiO_2 into the organic molecules adsorbed on TiO_2 surface. The photocatalytic reduction of aldehydes, nitro compounds, and imines have been reported. Aromatic aldehydes and ketones were reduced to the corresponding alcohols using TiO_2 as a photocatalyst [115, 116]. Aromatic and aliphatic nitro compounds were reduced to corresponding amines using TiO_2 as catalyst [117]. The direct reduction of imines to corresponding secondary amines was studied [118].

6. TiO_2 in health and biomedicine

6.1 TiO_2 in sunscreen

The sunlight reaching the earth's surface contains UV, visible and infrared wavelength. The Sun releases ultraviolet (UV) radiation in three different wavelengths, and all are harmful in different ways. These wavelengths in sunlight are called UVA (315–400 nm), UVB (280–315 nm) and UVC (100–280 nm) [119]. Because the earth's atmosphere blocks most UVC rays, UVC does not generally reach the earth's surface to a significant degree. Therefore, they are not thought to be important contributors to the biological effects on human skin [120]. UVA wavelength penetrates more deeply into the skin causing photo-aging and the formation of skin cancer. UVB is shorter, and damages the surface of the skin. The damage from UVB can cause sunburn and cancer [121–124].

TiO_2 is a semiconducting material with very high refractive index. The high refractive index is what allows the substance to scatter visible light. The current method of preventive treatment again harmful UV radiation involves suspending a substance that either absorbs or scatters UV radiation in a thick emulsion, called sunscreen. Titanium dioxide (TiO_2) is an ingredient in sunscreens where its loading is frequently 2–15%. Sunscreen typically contain chemical filters that are organic compounds that absorb strongly the UV (most often UVB) and physical filters such as TiO_2 and ZnO that block UVA and UVB sunlight through absorption, reflection and scattering.

6.2 TiO_2 for cancer treatment

In biomedicine, TiO_2 nanoparticles with their extraordinary stability, exceptional photo-reactivity, and biocompatibility have a special place in biomedical solutions. The therapeutic potential of TiO_2 lies in the ability of these particles in response to light to produce reactive oxygen species (ROS). Production of ROS is the main factor in causing detrimental effects on cells. This effect was first applied by Cai *et al* in the immortal HeLa cell lines [125]. Distinct cell death was detected after HeLa cells were illuminated with UV light in the presence of TiO_2 (100 μg/mL). TiO_2 particles in the absence of light showed little cytotoxicity for concentration as high as 360 μg/mL. This demonstrated that the cells were killed by radicals produced from water upon illumination of TiO_2 particles and also oxidized by the photogenerated holes in TiO_2. Because the size and shape of TiO_2 nanoparticles have strongly influence in crystallinity, surface characteristics, electron/hole transportation and charge separation, it is important to be able to control the shape and size of TiO_2 nanoparticles to optimize their electronic and chemical properties, resulting in more efficient site-selective reactions. Various functionalized TiO_2 nanoparticles have been designed to be used in nanomedicine, as agents for photosensitization or sonosensitization and as drug carriers [126].

In both photodynamic therapy (PDT) and sonodynamic therapy (SDT), nanostructured titanium dioxide is used as an agent to produce reactive oxygen species (ROS). Photodynamic therapy (PDT) is an anti-tumor method in which photosensitive agent is applied and target area is illuminated for the activation of the agent. TiO_2 is normally a photocatalyst that produces oxidizing radicals by reacting with water during UV exposure and can damage nearby cells [127, 128]. Titanium dioxide and zinc oxide are two of the most effective photosensitizers for PDT applications. In sonodynamic therapy, TiO_2 acts as a sonocatalyst. Studies have shown that TiO_2 particles can promote the production of hydroxyl ($OH^{\bullet}$) radicals by ultrasound irradiation even in dark conditions [129, 130]. Ultrasound technology has been already used for some cancer therapies, either by generating localized heating using high intensity ultrasound or by activating a drug release using low intensity ultrasound. Ultrasound can penetrate inches below the skin. Therefore, it can be used to activate TiO_2 nanoparticles deep below the skin surface.

TiO_2 has been considered to be a good material for the design of drug carriers, for the reasons that the shape and size of TiO_2 nanoparticles can be engineered to control their electronic and chemical properties, and the surface of TiO_2 nanoparticles can be functionalized with various drug molecules [131, 132]. These capabilities bring new opportunities for more efficient site-selective chemistry of TiO_2, and form the vehicles for drug delivery applications.

7. Conclusions

Titanium dioxide is a stable, non-toxic inorganic material with very high refractive index, and can scatter visible light almost completely. The particle sizes for pigmentary TiO_2 are generally engineered to be around 250 nm to have optimized light scattering property. After coating with inorganic compounds such as alumina or silica, the catalytic activity on the surface of TiO_2 particles is suppressed and the weather resistance is improved. Because of the superior optical properties and chemical stability, TiO_2 has been developed and used as white pigment over several decades. Pigmentary titanium dioxide has excellent ability to impart brightness and opacity. Titanium dioxide has now been a well established inorganic white pigment and is widely applied in the coatings, plastics, paper manufacturing, and in many common products. Global sales of titanium dioxide pigment were about 6 million tons in 2017 and the growth trend of global titanium dioxide pigment sales is continuing over the recent years.

Titanium dioxide is also a semiconducting material which is characterized by a filled valence band and an empty conduction band. When excited by photons which have energy equal to or higher than their band gap, electrons (e^-) in valence band of TiO_2 are promoted to the conduction band and holes (h^+) are created in the valence band of TiO_2. Because of the discovery of photocatalytic properties of titanium dioxide, and the ability to engineer TiO_2 nanomaterials for controlling their electronic and chemical properties, the applications of titanium dioxide as functional materials have become the focus of enormous research and development in the recent years. The applications of nano-structured TiO_2 can now be found in a wide range of areas including electronic materials, energy, environment, health & medicine, and catalysts. A number of materials containing nano-structured TiO_2 have become the important commercial products. Further research is continuing to modify the electronic and chemical properties, as well as surface characteristics of TiO_2 for the creation of more efficient TiO_2 functional materials in more specific application areas.

Acknowledgements

This work was financially supported by the Pangang Group under a Basic Research Grant.

Conflict of interest

The authors declare no conflict of interest.

Author details

Xiaoping Wu
Pangang Group Research Institute Co. Ltd., State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization, Panzhihua, Sichuan, China

*Address all correspondence to: 13308173290@163.com

References

[1] Winkler J. Titanium Dioxide, Production, Properties and Effectives Usage. 2nd ed. Hanover: Vincentz Network; 2013. 42p

[2] Chemours. Titanium Technologies Presentation [Internet]. 2018. Available from: https://s21.q4cdn.com/411213655/files/doc_presentations/2018/09/FINAL-September-2018-TT-Investor-Deck.pdf [Accessed: 2021-04-12]

[3] Kennedy D, Ritchie M, Mackenzie J. The photosorption of oxygen and nitric oxide on titanium dioxide. Transactions of the Faraday Society. 1958;54:119-129. DOI: 10.1039/TF9585400119

[4] Barry T, Stone F. The reactions of oxygen at dark and irradiated zinc oxide surfaces. Proceedings of the Royal Society A. 1960;255:124-144. DOI: 10.1098/rspa.1960.0058

[5] Doerffler W, Hauffe K. Heterogeneous photocatalysis I. The influence of oxidizing and reducing gases on the electrical conductivity of dark and illuminated zinc oxide surfaces. Journal of Catalysis. 1964;3:156-170. DOI: 10.1016/0021-9517(64)90123-X

[6] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972; 238:37-38. DOI: 10.1038/238037a0

[7] Linsebigler AL, Lu G, and Yates JT. Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chemical Reviews. 1995;95: 735-758. DOI: 10.1021/cr00035a013

[8] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chemical Reviews. 1995; 95:69-96. DOI: 10.1021/cr00033a004

[9] Wang R, Hashimoto K, Fujishima A, Chikuni M, Kojima E, Kitamura A, Shimohigoshi M, Watanabe T. Light-induced amphiphilic surfaces. Nature. 1997;388:431-432. DOI: 10.1038/41233

[10] Lakshmanan VI, Bhowmick A, Ha lim MA. In: Brown J, editor. Titanium Dioxide: Chemical Properties, Applications and Environmental Effects. New York: Science Publishers; 2014. p. 75-130

[11] Pierre AC, Pajonk GM. Chemistry of aerogels and their applications. Chemical Reviews. 2002;102:4243-4266. DOI: 10.1021/cr0101306

[12] Hench LL, West JK. The sol-gel process. Chemical Reviews. 1990;90: 33-72. DOI: 10.1021/cr00099a003

[13] Lee M, Lee G, Ju C, Hong S. Preparations of nanosized TiO_2 in reverse microemulsion and their photocatalytic activity. Solar Energy Materials and Solar Cells. 2005;88: 389-401. DOI: 10.1016/j.solmat.2004.11.010

[14] Schaf O, Ghobarkar H, Knauth P. Hydrothermal synthesis of nanomaterials. In: Knauth P, Shoonman J, editors. Nanostructured materials: selected synthesis methods, properties and applications. New York: Kluwer Academic Publishers; 2004. p. 23-41

[15] Wahi RK, Liu Y, Falkner JC, Colvin VL. Solvothermal synthesis and characterization of anatase TiO_2 nanocrystals with ultrahigh surface area. Journal of Colloid and Interface Science. 2006;302:530-536. DOI: 10.1016/j.jcis.2006.07.003

[16] Sivalingam G, Priya MH, Madra G. Kinetics of the photodegradation of substituted phenols by solution combustion synthesized TiO_2. Applied Catalysts B: Environmental.

2004;51:67-76. DOI: 10.1016/j.apcatb.2004.02.006

[17] Byun D, Jin B, Kim J, Lee JK, Park D. Photocatalytic TiO_2 deposition by chemical vapor deposition. Journal of Hazardous Materials. 2000;73: 199-206. DOI: 10.1016/S0304-3894(99)00179-X

[18] Miyata T, Tsukada S, Minami T. Preparation of anatase TiO_2 thin films by vacuum arc plasma evaporation Thin Solid Films. 2006;496:136-140. DOI: 10.1016/j.tsf.2005.08.294

[19] Gazquez M, Bolivar J, Tenorio R, Vaca F. A Review of the production cycle of titanium dioxide pigment. Materials Science and Applications. 2014;5:441-458. DOI: 10.4236/msa.2014.57048

[20] Linak E, Inoguchi Y. Chemical economics handbook: titanium dioxide. SRI Consulting, Menlo Park. 2005

[21] Braun JH, Baidins A, Marganski RE. TiO_2 pigment technology: a review. Progress in Organic Coatings. 1992;20: 105-138. DOI: 10.1016/0033-0655(92)80001-D

[22] Hadjiivanov KI, Klissurski DG. Surface chemistry of titania (anatase) and titania-supported catalysts. Chemical Society Reviews. 1996;25: 61-69. DOI: 10.1039/CS9962500061

[23] M. Grätzel. Conversion of sunlight to electric power by nanocrystalline dye sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry. 2004;164:3-14. DOI: 10.1016/j.jphotochem.2004.02.023

[24] Ni M, Leung M, Sumathy K. A review and recent developments in photocatalytic water-splitting using TiO_2 for hydrogen production. Renewable and Sustainable Energy Reviews. 2007;11:401-425. DOI: 10.1016/j.rser.2005.01.009

[25] Grätzel M. Photoelectrochemical cells. Nature. 2001;414:338344. DOI: 10.1038/35104607

[26] O'Regan B, Grätzel M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. Nature. 1991;353:737-740. DOI: 10.1038/353737a0

[27] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han L. Dye-sensitized solar cells with conversion efficiency of 11.1%. Japanese Journal of Applied Physics. 2006;45:L638-640. DOI: 10.1143/JJAP.45.L638

[28] Yu Q, Wang Y, Yi Z, Zu N, Zhang J, Zhang M, Wang P. high-efficiency dye-sensitized solar cells: the influence of lithium ions on exciton dissociation, charge recombination, and surface states. ACS Nano. 2010;4:6032-6038. DOI: 10.1021/nn101384e

[29] Smestad G, Bignozzi C, Argazzi R. Testing of dye sensitized TiO_2 solar cells I: Experimental photocurrent output and conversion efficiencies. Solar Energy Materials and Solar Cells. 1994; 32:259-272. DOI: 10.1016/0927-0248(94)90263-1

[30] Kay A, Grätzel M. Low cost photovoltaic modules based on dye sensitized nanocrystalline titanium dioxide and carbon powder. Solar Energy Materials and Solar Cells. 1996; 44:99-117. DOI: 10.1016/0927-0248(96)00063-3

[31] Hagfeldt A, Grätzel M. Molecular Photovoltaics. Accounts of Chemical Research. 2000;33:269-277. DOI: 10.1021/ar980112j

[32] Nazeeruddin MK, Angelis FD, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B, Grätzel M. Combined experimental and DFT-TDDFT computational study of photoelectrochemical cell ruthenium sensitizers. Journal of American

Chemical Society. 2005;127: 16835-16847. DOI: 10.1021/ja052467l

[33] Cao Y, Bai Y, Yu Q, Cheng Y, Liu S, Shi D, Gao F, Wang P. Dye-sensitized solar cells with a high absorptivity ruthenium sensitizer featuring a 2-(hexylthio)thiophene conjugated bipyridine. The Journal of Physical Chemistry C. 2009;113:6290-6297. DOI: 10.1021/jp9006872

[34] Green MA, Hishikawa Y, Dunlop ED, Levi DH, Hohl-Ebinger J, Ho-Baillie A. Solar cell efficiency tables (version 51). Progress in Photovoltaics. 2018;26:3-12. DOI: 10.1002/pip.2978

[35] Kim HS, Kim HS, Lee CR, Im JH, Lee KB, Moehl T, Marchioro A, Moon SJ, Humphry BR, Yum JH, Moser JE, Grätzel M, Park N.G. lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%. Scientific Reports. 2012;2:591-597. DOI: 10.1038/srep00591

[36] Heo J, Im S, Noh J, et al. Efficient inorganic–organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. The Nature Photonics. 2013;7:486-491. DOI: 10.1038/nphoton.2013.80

[37] Burschka J, Burschka J, Pellet N, Moon S, Humphry-Baker R, Gao P, Nazeeruddin MK, Grätzel M. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature. 2013;499:316-319. DOI: 10.1038/nature12340

[38] Fujishima A, Rao TN, Tryk DA. Titanium Dioxide Photocatalysis. Journal of Photochemistry and Photobiology. C. 2000;1:1-21. DOI: 10.1016/S1389-5567(00)00002-2

[39] Tryk DA, Fujishima A, Honda K. Recent topics in photoelectrochemistry: achievements and future prospects. Electrochimica Acta. 2000;45: 2363-2376. DOI: 10.1016/S0013-4686(00)00337-6

[40] Bamwenda GR, Tsubota S, Nakamura T, Haruta M. Photoassisted hydrogen production from a water ethanol solution: a comparison of activities of Au-TiO_2 and Pt-TiO_2. Journal of Photochemistry and Photob iology A: Chemistry. 1995;89:177-189. DOI: 10.1016/1010-6030(95)04039-I

[41] Sakthivel S, Shankar MV, Palanichamy M, Arabindoo B, Bahnemann DW, Murugesan V. Enhancement of photocatalytic activity by metal deposition: characterization and photonic efficiency of Pt, Au and Pd deposited on TiO_2 catalyst. Water Research. 2004;38:3001-3008. DOI: 10.1016/j.watres.2004.04.046

[42] Li FB, Li XZ. The enhancement of photodegradation efficiency using Pt-TiO_2 catalyst. Chemosphere, 2002;48: 1103-1111. DOI: 10.1016/S0045-6535(02)00201-1

[43] Kim S, Choi W. Dual photocatalytic pathways of trichloroacetate degradation on TiO_2: effects of Nanosized platinum deposition on kinetics and mechanism. The Journal of Physical Chemistry B. 2002;106: 13311-13317. DOI: 10.1021/jp0262261

[44] Park JH, Kim S, Bard AJ. Novel carbon-doped TiO_2 nanotube arrays with high aspect ratios for efficient solar water splitting. Nano Letter. 2006;6: 24-28. DOI: 10.1021/nl051807y

[45] Dhanalakshmi KB, Latha S, Anandan S, Maruthamuthu P. Dye sensitized hydrogen evolution from water. International Journal of Hydroge n Energy. 2001;26:669-674. DOI: 10.1016/S0360-3199(00)00134-8

[46] Yan H, Yang H. TiO_2–g-C_3N_4 composite materials for photocatalytic H_2 evolution under visible light

irradiation. Journal of Alloys and Compounds. 2011;509: L26-L29. DOI: 10.1016/j.jallcom.2010.09.201

[47] Kavan L. Electrochemistry of titanium dioxide: some aspects and highlights. Chem. Record. 2012;12:131-142. DOI: 10.1002/tcr.201100012

[48] Yang Z, Choi D, Kerisit S, Rosso KM, Wang D, Zhang J, Graff G, Liu J. Nanostructures and lithium electrochemical reactivity of lithium titanites and titanium oxides: A review. Journal of Power Sources. 2009;192: 588-598. DOI: 10.1016/j.jpowsour.2009.02.038

[49] Li X, Zhang Y, Li T, Zhong Q, Li H, Huang J. Graphene nanoscrolls encapsulated TiO_2 (B) nanowires for lithium storage. Journal of Power Sources. 2014;268:372-378. DOI: 10.1016/j.jpowsour.2014.06.056

[50] Jin J, Huang S, Liu J, Li Y, Chen D, Wang H, Yu Y, Chen L, Su B. Design of new anode materials based on hierarchical, three dimensional ordered macromesoporous TiO_2 for high performance lithium ion batteries. Journal of Materials Chemistry A. 2014; 2:9699-9708, 2014. DOI: 10.1039/c4ta01775g

[51] Murphy DW, Cava RJ, Zahurak SM, Santoro A. Ternary $LixTiO_2$ phases from insertion reactions. Solid State Ionics. 1983;9-10:413-417. DOI: 10.1016/0167-2738(83)90268-0

[52] Zachau-Christiansen B, West K, Jacobsen T, Atlung S. Lithium insertion in different TiO_2 modifications. Solid State Ionics. 1988;28:1176-1182. DOI: 10.1016/0167-2738(88)90352-9

[53] Dambournet D, Belharouak I, Amine K. Tailored preparation methods of tio_2 anatase, rutile, brookite: mechanism of formation and electrochemical properties. Chemistry of Materials. 2010;22:1173-1179. DOI: 10.1021/cm902613h

[54] Tammawat P, Meethong N. Synthesis and characterization of stable and binder-free electrodes of TiO_2 nanofibers for Li ion batteries. Journal of Nanomaterials. 2013. Article ID 413692. 8 pages. DOI: 10.1155/2013/413692

[55] Chen J, Liu H, Qiao S, and Lou X. Carbon-supported ultra-thin anatase TiO_2 nanosheets for fast reversible lithium storage. Journal of Materials Chemistry. 2011;21:5687-5692. DOI: 10.1039/C0JM04412A

[56] Chen J, Lou X. Anatase TiO_2 nanosheet: an ideal host structure for fast and efficient lithium insertion/extraction. Electrochemistry Communications. 2009;11:2332-2335. DOI: 10.1016/j.elecom.2009.10.024

[57] Nguyen-Phan TD, Pham VH, Kweon H, et al. Uniform distribution of TiO_2 nanocrystals on reduced graphene oxide sheets by the chelating ligands. Journal of Colloid and Interface Science. 2012;367:139-147. DOI: 10.1016/j.jcis.2011.10.021

[58] Winter M, Brodd RJ. What are batteries, fuel cells and supercapacitors?. Chemical Reviews. 2004;104: 4245-4244. DOI:10.1021/cr020730k

[59] Whittingham MS, Savinell RF, Zawodzinski T. Introduction: Batteries and Fuel Cells. Chemical Reviews. 2004; 104:4243-4244. DOI: 10.1021/cr020705e

[60] Subramamian V, Karki A, Gnansekra KI, Eddy FP, Rambabu B. Nanocrystalline TiO_2 (anatase) for Li-ion batteries. Journal of Power Sources. 2006;159:219-222. DOI: 10.1016/j.jpowsour.2006.04.027

[61] Zang Y, Zhang Z, Gong Z. Electrochemical performance and surface properties of bare and

TiO_2-coated cathode materials in lithium-ion batteries. Journal of Physical Chemistry B. 2004;108:17546-17552. DOI: 10.1021/jp046980h

[62] Huang H, Zhang WK, Gan XP, Wang C, Zhang L. Electrochemical investigation of TiO_2/carbon Nanotubes nanocomposite as anode materials for lithium-ion batteries. Material Letters. 2007;61:296-299. DOI: 10.1016/j.matlet.2006.04.053

[63] Fu L, Liu H, Zhang H, Li C, Zhang T, Wu Y, Wu H. Novel TiO_2/C nanocomposites for anode materials of lithium-ion batteries. Journal of Power Sources. 2006;159:219-222. DOI: 10.1016/j.jpowsour.2006.04.081

[64] Park S, Seo S, Lee S, Seo S. Sb: SnO_2@TiO_2 heteroepitaxial branched nanoarchitectures for Li ion battery electrodes. The Journal of Physical Chemistry C. 2012; 116:21717-21726. DOI: 10.1021/jp308077a

[65] Wu X, Zhang S, Wang L, Du Z, Fang H, Ling Y, Huang Z. Coaxial SnO_2@TiO_2 nanotube hybrids: from robust assembly strategies to potential application in Li^+ storage. Journal of Materials Chemistry. 2012; 22: 11151-11158. DOI: 10.1039/C2JM30885A

[66] Guan C, Wang X, Zhang Q, Fan Z, Zhang H, Fan H. Highly stable and reversible lithium storage in SnO_2 nanowires surface coated with a uniform hollow shell by atomic layer deposition. Nano Letters. 2014;14: 4852-4858. DOI: 10.1021/nl502192p

[67] Jeun J, Park K, Kim D, Kim W, Kim H, Lee B, Kim H, Yu W, Kanga K, Hong S. SnO_2@TiO_2 double shell nanotubes for a lithium ion battery anode with excellent high rate cyclability. Nanoscale. 2013;5: 8480-8483. DOI: 10.1039/C3NR01964K

[68] Daneshvar N, Salari D, Khataee AR. Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. Journal of Photochemistry and Photobiology A: Chemistry. 2003;157:111-116. DOI: 10.1016/S1010-6030(03)00015-7

[69] Daneshvar N, Salari D, Niaie A, Rasoulifard MH. A. R. Khataee. Immobilization of TiO_2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye c.i. direct red 23. Journal of Environmental Science and Health, Part A. 2005;40: 1605-1617. DOI: 10.1081/ESE-200060664

[70] Tachikawa T, Majima T. Single-molecule fluorescence imaging of tio_2 photocatalytic reactions. Langmuir. 2009;25:7791-7802. DOI: 10.1021/la900790f

[71] Daneshvar N, Aleboyeh A, Khataee AR. The evaluation of electrical energy per order (E_{Eo}) for photooxidative decolorization of four textile dye solutions by the kinetic model. Chemosphere. 2005;59:761-767. DOI: 10.1016/j.chemosphere.2004.11.012

[72] Loddo V, Marcì G, Martı́n C, Palmisano L, Rives V, Sclafania A. Preparation and characterisation of TiO_2 (anatase) supported on TiO_2 (rutile) catalysts employed for 4-nitrophenol photodegradation in aqueous medium and comparison with TiO_2 (anatase) supported on Al_2O_3. Applied Catalysis B: Environmental. 1999;20:29-45. DOI: 10.1016/S0926-3373(98)00089-7

[73] Bakardjieva S, Subrt J, Stengl V, Dianez M, Sayagues M. Photoactivity of anatase-rutile TiO_2 nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase. Applied Catalysis B: Environmental. 2005;58:193-202. DOI: 10.1016/j.apcatb.2004.06.019

[74] Beydoun D, Amal DR, Low G, McEvoy S. Role of nanoparticles in

photocatalysis. Journal of Nanoparticles Research. 1999;1:439-458. DOI: 10.1023/A:1010044830871

[75] Henglein A. Small-particle research: physicochemical properties of extremely small colloidal metal and semiconductor particles. Chemical Reviews. 1989;89:1861-1873. DOI: 10.1021/cr00098a010

[76] Guan K. Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of TiO_2/SiO_2 films. Surface and Coating Technology. 2005;191:155-160. DOI: 10.1016/j.surfcoat.2004.02.022

[77] Fujishima A, Zhang A. Titanium dioxide photocatalysis: present situation and future approaches. Comptes Rendus Chimie. 2006;9:750-760. DOI: 10.1016/j.crci.2005.02.055

[78] Cheng Q, Li C, Pavlinek V, Saha P, Wang H. Surface-modified antibacterial TiO_2/Ag^+ nanoparticles: Preparation and properties. Applied Surface Science. 2006;252:4154-4160. DOI: 10.1016/j.apsusc.2005.06.022

[79] Trapalis C, Keivanidis P, Kordas G, Zaharescu M, Crisan M, Szatvanyi A, Gartner M. Nanostructured thin films with antibacterial properties. Thin Solid Films. 2003;433:186-190. DOI: 10.1016/S0040-6090(03)00331-6

[80] Zhang H, Wen D. Antibacterial properties of Sb-TiO_2 thin films by RF magnetron co-sputtering. Surface & Coating Technology. 2007;201: 5720-5723. DOI: 10.1016/j.surfcoat.2006.07.109

[81] Yuranova T, Laub D, Kiwi J. Synthesis, activity and characterization of textiles showing self-cleaning activity under daylight irradiation. Catalysis Today. 2007;122:109-117. DOI: 10.1016/j.cattod.2007.01.040

[82] Mills A, Lepre A, Elliott N, Bhopal S, Parkin IP, O'Neill S. Characterisation of the photocatalyst Pilkington Activ (TM): a reference film photocatalyst? Journal of Photochemistry and Photobiology A: Chemistry. 2003;160: 213-224. DOI: 10.1016/S1010-6030(03)00205-3

[83] Ashkarran A, Aghigh S, Kavianipour M, Farahani N. Visible light photo-and bioactivity of Ag/TiO_2 nanocomposite with various silver contents. Current Applied Physics. 2011;11:1048-1055. DOI: 10.1016/j.cap.2011.01.042

[84] Cotolan N, Rak M, Bele M, Cör A, Muresan LM, Milošev I. Sol-gel synthesis, characterization and properties of TiO_2 and Ag-TiO_2 coatings on titanium substrate. Surface & Coating Technology. 2016;307:790-799. DOI: 10.1016/j.surfcoat.2016.09.082

[85] Liu C, Geng L, Yu Y, Zhang Y, Zhao B, Zhao Q. Mechanisms of the enhanced antibacterial effect of Ag-TiO_2 coatings. Biofouling. 2018;34:190-199. DOI: 10.1080/08927014.2017.1423287

[86] Pilkington. self-clean glass [Internet]. 2021. Available from: https://www.pilkington.com/en-gb/uk/householders/types-of-glass/self-cleaning-glass. [Accessed: 2021-04-08]

[87] Kallio T, Alajoki S, Pore V, Ritala M, Laine J, Leskela M, Stenius P. Antifouling properties of TiO_2: Photocatalytic decomposition and adhesion of fatty and rosin acids, sterols and lipophilic wood extractives. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2006;29:162-176. DOI: 10.1016/j.colsurfa.2006.06.044

[88] Piranniemi M, Sillanpaa M. Heterogeneous water phase catalysis as an environmental application: a review. Chemosphere. 2002;48:1047-1060. DOI: 10.1016/S0045-6535(02)00168-6

[89] Carp O, Huisman CL, Reller A. Photoinduced reactivity of titanium

dioxide. Progress in Solid State Chemistry. 2004;32:33-177. DOI: 10.1016/j.progsolidstchem.2004.08.001

[90] Wang Y, Huang Y, Ho W, Zhang L, Zou Z, Lee S. Biomolecule-controlled hydrothermal synthesis of C–N–S-tridoped TiO_2 nanocrystalline photocatalysts for NO removal under simulated solar light irradiation. Journal of Hazardous Materials. 2009;169:77-87. DOI: 10.1016/j.jhazmat.2009.03.071

[91] Frank SN, Bard AJ. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solutions at titanium dioxide powder. Journal of the American Chemical Society. 1977;99:303-304. DOI: 10.1021/ja00443a081

[92] Frank SN, Bard AJ. Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders. Journal of Physical Chemistry. 1977;81:1484-1488. DOI: 10.1021/j100530a011

[93] Konstantinou IK, Albanis TA. TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. Applied Catalysis B: Environmental. 2004;49:1-14. DOI: 10.1016/j.apcatb.2003.11.010

[94] Molinari R, Pirillo F, Loddo V, Palmisano L. Heterogeneous photocatalytic degradation of pharmaceuticals in water by using polycrystalline TiO_2 and a nanofiltration membrane reactor. Catalysis Today. 2006;118:205-213. DOI: 10.1016/j.cattod.2005.11.091

[95] Li L, Zhu P, Zhang P, Chen Z, Han W. Photocatalytic oxidation and ozonation of catechol over carbon-black-modified nano-TiO_2 thin films supported on Al sheet. Water Research. 2003;37:3646-3651. DOI: 10.1016/S0043-1354(03)00269-0

[96] Fu W, Yang H, Chang L, Bala H, Li M, Zou G. Anatase TiO_2 nanolayer coating on strontium ferrite nanoparticles for magnetic photocatalyst. Colloids and Surfaces A: Physicochemical Engineering Aspects. 2006;289:47-52. DOI: 10.1016/j.colsurfa.2006.04.013

[97] Ismail AA, Bahnemann DW. Mesoporous titania photocatalysts: preparation, characterization and reaction mechanisms. Journal of Materials Chemistry. 2011;21:11686-11707. DOI: 10.1039/C1JM10407A

[98] Di Paola A, Carcia-Lopez E, Marci E, Palmisano L. A survey of photocatalytic materials for environmental remediation. Journal of Hazardous Materials. 2012;211-212:3-29. DOI: 10.1016/j.jhazmat.2011.11.050

[99] Fujishima A, Zhang X, Tryk DA. TiO_2 photocatalysis and related surface phenomena. Surface Science Reports. 2008;63:515-582. DOI: 10.1016/j.surfrep.2008.10.001

[100] Emeline AV, Kuznetsov VN, Rybchuk VK, Serpone N. Visible-light-active titania photocatalysts: the case of N-doped TiO_2-properties and some fundamental issues. International Journal of Photoenergy. 2008;Article ID 258394:19 pages. DOI: 10.1155/2008/258394

[101] Irie H, Watanabe Y, Hashimoto K. Carbon-doped anatase TiO_2 powders as a visible-light sensitive photocatalyst. Chemistry Letters. 2003;32:772-773. DOI: 10.1246/cl.2003.772

[102] Sakthivel S, Kisch H, Daylight Photocatalysis by Carbon-modified titanium dioxide. Angewandte Chemie International Edition. 2003;42:4908-4911. DOI: 10.1002/anie.200351577

[103] Morikawa T, Asahi R, Ohwaki T, Aoki K, Taga Y. Band-gap narrowing of titanium dioxide by nitrogen doping.

Japanese Journal of Applied Physics. 2001;40:L561-L563. DOI: 10.1143/JJAP.40.L561

[104] Primo A, Corma A, Garcia H. Titania supported gold nanoparticles as photocatalyst. Physical Chemistry Chemical Physics. 2011;13:886-910. DOI: 10.1039/C0CP00917B

[105] Smirniotis PG, Donovan AP, Uphade BS. Low-temperature selective catalytic reduction (SCR) of NO with NH_3 by using Mn, Cr, and Cu oxides supported on Hombikat TiO_2. Angewandte Chemie International Edition. 2001;40:2479-2482. DOI: 10.1002/1521-3773(20010702)40:13 <2479::AID-ANIE2479>3.0.CO;2-7

[106] Nakajima F, Hamada. The state-of-the-art technology of NOx control, Catalysis Today. 1996;29:109-115. DOI: 10.1016/0920-5861(95)00288-X

[107] Huang H, Long R, Yang R. A highly sulfur resistant Pt-Rh/TiO/Al_2O_3 storage catalyst for NOx reduction under lean-rich cycles, Applied Catalysis B: Environmental. 2001;33:127-136. DOI: 10.1016/S0926-3373(01)00176-X.

[108] Busca G, Lietti L, Ramis G, Berti F. Chemical and mechanistic aspects of the selective catalytic reduction of NOx by ammonia over oxide catalysts: A review. Applied Catalysis B: Environmental. 1998;18:1-36. DOI: 10.1016/S0926-3373(98)00040-X

[109] Dunn JP, Stenger HG, Wachs IE. Oxidation of sulfur dioxide over supported vanadia catalysts: molecular structure-reactivity relationships and reaction kinetics. Catalysis Today. 1999;51:301-318. DOI: 10.1016/S0920-5861(99)00052-8

[110] Lai J, Wachs IE. A perspective on the selective catalytic reduction (SCR) of NO with NH_3 by supported V_2O_5-WO_3/TiO_2 catalysts. ACS Catalysis. 2018;8:6537-6551. DOI: 10.1021/acscatal.8b01357

[111] Boonstra AH, Mutsaers CA. Photohydrogeneration of ethyne and ethene on the surface of titanium dioxide. Journal of Physical Chemistry. 1975;79:2025-2027. DOI: 10.1021/j100586a009

[112] Yun C, Anpo M, Kodama S, Kubokawa Y. U.V. Irradiation-induced fission of a C=C or C≡C bond adsorbed on TiO_2. Journal of Chemical Society, Chemical Communications. 1980;609-609. DOI: 10.1039/C39800000609

[113] Baba R, Nakabayashi S, Fujishima A, Honda K. Photocatalytic hydrogenation on the bimetal-deposited semiconductors powders. Journal of the American Chemical Society. 1987;109:2273-2277. DOI: 10.1021/ja00242a007

[114] Kanno T, Oguchi T, Sakuragi H, Tokumaru K, Semiconductor-catalyzed photooxygenation of aromatic olefins, Tetrahedron Letters. 1980;21:467-470. DOI: 10.1016/S0040-4039(00)71435-3

[115] Joyce-Pruden C, Pross JK, Li Y. Photoinduced reduction of aldehydes on titanium dioxide. Journal of Organic Chemistry. 1992;57:5087-5091. DOI: 10.1021/jo00045a018

[116] Kohtani S, Yoshioka E, Saito K, Kudo A, Miyabe H. Photocatalytic hydrogenation of acetophenone derivatives and diary ketones on polycrystalline titanium dioxide. Catalysis Communications. 2010;11:1049-1053. DOI: 10.1016/j.catcom.2010.04.022

[117] Mahdavi F, Brudon TC, Li Y. Photoinduced reduction of nitro compounds on semiconductor particulates. Journal of Organic Chemistry. 1993;58:744-746. DOI: 10.1021/jo00055a033

[118] Ohtani B, Goto Y, Nishimoto S, Inui T. Photocatalytic transfer hydrogenation of Schiff Bases with propan-2-ol by suspended semiconductor particles loaded with

platinum deposits. Journal of the Chemical Society, Faraday Transactions. 1996;92:4291-4295. DOI: 10.1039/FT9969204291

[119] Urbach F. The historical aspects of sunscreens. Journal of Photochemistry and Photobiology B: Biology. 2001;64: 99-104. DOI: 10.1016/S1011-1344(01)00202-0

[120] Gallagher RP, Lee TK. Adverse effects of ultraviolet radiation: A brief review. Progress in Biophysics and Molecular Biology. 2006;92:119-131. DOI: 10.1016/j.pbiomolbio.2006.02.011

[121] Mansoori GA, Mohazzabi P, McCormack P, Jabbari S. Nanotechnology in cancer prevention, detection and treatment: bright future lies ahead. World Review of Science, Technology and Sustainable Development. 2007;4:226-257. DOI: 10.1504/WRSTSD.2007.013584

[122] Shen B, Scaiano JC, English M. Zeolite encapsulation TiO_2-photosensitized ROS generation in cultured human skin fibroblasts, Photochemistry and photobiology. 2006; 82:5-12. DOI: 10.1562/2005-05-29-RA-551

[123] Dondi D, Albini A, Serpone N. Interactions between different solar UVB/UVA filters contained in commercial suncreams and consequent loss of UV protection, Photochemistry and Photobiology Science. 2006;5: 835-843. DOI: 10.1039/B606768A

[124] Morsella M, d'Alessandro N, Lanterna A, Scaiano J. Improving the sunscreen properties of TiO_2 through an understanding of its catalytic properties. ACS Omega. 2016;1:464–469. DOI: 10.1021/acsomega.6b00177

[125] Cai R, Hashimoto K, Itoh K, Kubota Y, Fujishima A. Photokilling of malignant cells with ultrafine TiO_2 powder. Bulletin of the Chemical Socie ty of Japan. 1991;64:1268-1273. DOI: 10.1246/bcsj.64.1268

[126] Rajh T, Dimitrijevic N, Bissonnette M, Koritarov T, Konda V. Titanium dioxide in the service of the biomedical revolution. Chemical Reviews. 2014;114:10177–10216. DOI: 10.1021/cr500029g

[127] Liu L, Miao P, Xu Y, Tian Z, Zou Z, Li G. Study of Pt/TiO_2 nanocomposite for cancer-cell treatment. Journal of Ph otochemistry and Photobiology B: Biology. 2010;98:207–210. DOI: 10.1016/j.jphotobiol.2010.01.005

[128] Çeşmeli S, Avci C. Application of titanium dioxide (TiO_2) nanoparticles in cancer therapies. Journal of Drug Targeting. 2018;27:762-766. DOI: 10.1080/1061186X.2018.1527338

[129] Ninomiya K, Ogino C, Oshima S, Sonoke S, Kuroda S Shimizu N. Targeted sonodynamic therapy using protein-modified TiO_2 nanoparticles. Ultrasonic s Sonochemistry. 2012;19:607-614. DOI: 10.1016/j.ultsonch.2011.09.009

[130] Yamaguchi S, Kobayashi H, Narita T, Kanehira K, Sonezaki S, Kudo N, Kubota Y, Terasaka S, Houkin K. Sonodynamic therapy using water-dispersed TiO_2-polyethylene glycol compound on glioma cells: Comparison of cytotoxic mechanism with photodynamic therapy. Ultrasonics Sonochemistry. 2011;18:1197-1204. DOI: 10.1016/j.ultsonch.2010.12.017

[131] Wang T, Jiang H, Wan L, Zhao Q, Jiang T, Wang B, Wang S. Potential application of functional porous TiO_2 nanoparticles in light-controlled drug release and targeted drug delivery, Acta Biomaterialia. 2015;13:354-363. DOI: 1016/j.actbio.2014.11.010

[132] Wang Q, Huang J, Li H, Chen Z, Zhao Z, Wang Y, Zhang K, Sun H, Al-Deyab S, Lai Y. TiO_2 nanotube platforms for smart drug delivery: a review. International Journal of Na nomedicine. 2016;11:4819-4834. DOI: 10.2147/IJN.S108847